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1		Cog. Eng. B. C. CARPENTER	<i>Brad Carpenter</i>	10/24/94		Proj. S. J. EBERLEIN	<i>S. J. Eberlein</i>	10/24/94		1	1
1		Cog. Mgr. C. S. HALLER	<i>R. D. Haller</i>	10/20/94		Proj. J. W. OSBORNE	<i>J. W. Osborne</i>	10/20/94		1	1
1	1	QA K. K. KELLER	<i>Don Keller</i>	10-21-94		Proj. D. L. EDWARDS	<i>Don Edwards</i>	10/21/94		1	1
		Safety									
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18. B. C. CARPENTER <i>Brad Carpenter</i> Signature of EDT Originator Date 10/24/94		19. S. J. EBERLEIN <i>S. J. Eberlein</i> Authorized Representative for Receiving Organization Date 10-21-94		20. C. S. HALLER <i>R. D. Haller</i> Cognizant Manager Date 10/20/94		21. DOE APPROVAL (if required) Ctrl. No. <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments	
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APPROVED FOR PUBLIC RELEASE		
7. Abstract This document is a plan which serves as the contractual agreement between the Characterization Program, Sampling Operations, WHC 222-S Laboratory, Oak Ridge National Laboratory, and PNL 329 Laboratory. The scope of this plan is to provide guidance for the sampling and analysis of vapor samples from tank 241-BY-108.		
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WHC-SD-WM-TP-275
Revision 0

Tank 241-BY-108 Tank Characterization Plan

Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management

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LIST OF ACRONYMS

BY-108	Tank 241-BY-108
DQO	data quality objective
EPA	Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HEPA	high efficiency particulate air
ISS	in-situ sampling
ppbv	parts per billion by volume
ppmv	parts per million by volume
RCRA	Resource Conservation and Recovery Act
SACS	Surveillance Analysis Computer System
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TO-12	EPA task order protocol 12
TO-14	EPA task order protocol 14
TOC	total organic carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

TANK 241-BY-108 TANK CHARACTERIZATION PLAN

1.0 SPECIFIC TANK CHARACTERIZATION OBJECTIVES

The sampling and analytical needs associated with the 51 Hanford Site underground storage tanks classified on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat), and the safety screening of all 177 tanks have been identified through the Data Quality Objective (DQO) process. DQO's identify information needed by a program group in the Tank Waste Remediation System concerned with safety issues, regulatory requirements, or the transporting and processing of tank waste.

This Tank Characterization Plan will identify characterization objectives for tank BY-108 pertaining to sample collection, sample preparation and analysis, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Waste Remediation System Tank Waste Analysis Plan* (Haller 1994) and the applicable Data Quality Objectives identified in the following sections. In addition, an estimate of the current contents and status of the tank is given.

1.1 Tank Safety Screening Data Quality Objectives

The *Tank Safety Screening Data Quality Objective* (Redus and Babad 1994) describes the sampling and analytical requirements that are used to screen waste tanks for unidentified safety issues. Both Watch List and non-Watch List tanks will be sampled and evaluated to identify tank safety conditions related to the four Watch-List safety issues and classify the waste tanks into one of three categories: SAFE, CONDITIONALLY SAFE, or UNSAFE. A tank can be removed from the a Watch List if it is classified as SAFE. The safety screening analyses shall be applied to all core samples, DST RCRA samples, and all auger samples, except auger samples taken exclusively to assess the flammable gas tank crust burn issue.

To meet the sampling requirements of this DQO effort, a vertical profile of the waste shall be obtained from at least two widely-spaced risers. This vertical profile may be realized using core, auger, or grab samples. The analytical requirements are concerned with measuring four primary analytes: energetics, total alpha activity, moisture level, and flammable gas concentration. If a specific criteria level on one of these items is exceeded, further analysis of a secondary set of analytes and a possible CONDITIONALLY SAFE or UNSAFE tank classification would be warranted.

1.2 Health and Safety Vapor Issue Resolution Data Quality Objectives

The *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a) concerns the tanks on the current "Suspect Tank List" and describes the methodology used to: 1) identify those tanks which can safely be sampled with intrusive equipment without risk of gas ignition; and 2) identify and estimate concentrations of toxicologically significant compounds present in the tank headspace and compare to published (if available) exposure limits.

1.3 Vapor Sampling Data Quality Objectives to Support Rotary Core Sampling

A portable modular exhauster has been developed to exhaust the tank atmosphere during a rotary drill sampling operation. Characterization of the tank headspace is needed to support exhauster start-up and define operational monitoring parameters. The *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994) defines requirements needed to identify the potential for release of regulated pollutants, confirm that the exhauster can be safely started, and establish alarm setpoints for total organic carbon (TOC) and ammonia release to maintain safe exhauster operation. To start the exhauster, the flammability and concentration of toxic gases in the tank vapor space is needed.

1.4 Ferrocyanide Safety Issue Data Quality Objectives

The *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objective Process* (Meacham et al. 1994) identifies the requirements needed to determine total fuel and moisture content for tanks on the Ferrocyanide Watch List, including tank BY-108.

1.5 Organic Fuel Rich Safety Issue Data Quality Objectives

The *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al., 1994) identifies requirements used to determine which classification to place a tank, based on analyses that establish if organic carbon and moisture content are above or below an established threshold. The primary analyses employed are organic carbon, presence of a free organic liquid phase, moisture content, and tank temperature. If the primary analyses are close to the threshold, the concentration of secondary analytes such as major organic species, certain oxidizing agents, hydroxide level, or radiochemical species may be needed.

2.0 RELEVANT SAFETY INFORMATION

The organic safety arises due to wastes added to SSTs containing quantities of complexants used in waste management operations, as well as degradation products of these complexants and solvents used in fuel reprocessing and metal recovery operations. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite/nitrate oxidizers that are sufficient to exothermally oxidize organic compounds.

The relevant safety issues with tanks on the Ferrocyanide Watch List concern 1) the potential for a propagating reaction between complexes of ferrocyanide and nitrate and nitrite that could result in a release of radioactive material, and 2) the possibility that other, as yet unidentified, safety issues exist for the tank.

Vapor samples are used to identify potential flammable and fugitive vapor emissions from the tanks which could become worker health and safety issues.

2.1 Tank Status

Single-shell tank BY-108 is classified as a Ferrocyanide Watch List tank. The tank was declared an assumed leaker and removed from service in

1972; interim stabilized was completed in February 1985. To prevent further waste addition intrusion prevention was completed (Hanlon 1994). Although not officially an Organic Watch List tank, restrictions have been placed on intrusive operations by Standing Order #94-16 (dated 09/08/94) since the tank is suspected to contain or to have contained a floating organic layer.

Tank BY-108 is estimated to contain 625,000 liters (165,000 gal.) of sludge and 238,000 liters (63,000 gal.) of saltcake with no pumpable or drainable liquid for a total of 863,000 liters (228,000 gal.). The median temperature of the waste in tank BY-108 is 29°C; the maximum temperature is 68°C (Brevick et al. 1994). The saltcake is estimated to contain 34,000 liters (9,000 gal.) of interstitial liquid. Its contents are categorized as non-complexed waste (Hanlon 1994).

Recent readings (July, 1994) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System (SACS) database indicate a waste depth of 87.5 inches below riser 4, which is located on the north side approximately 1/3 of the radius from the center of the tank. From this, the total waste volume is calculated at 833,000 liters (220,000 gal.).

2.2 Tank Monitoring Activities

Waste level measurements are taken on a quarterly basis through riser 4 using a manual tape. Internal tank temperature is automatically recorded from 13 thermocouples on a tree in riser 1. Six active dry wells monitor radiation in the surrounding soil (Brevick et al. 1994).

3.0 SUMMARY OF HISTORICAL INFORMATION FOR TANK BY-108

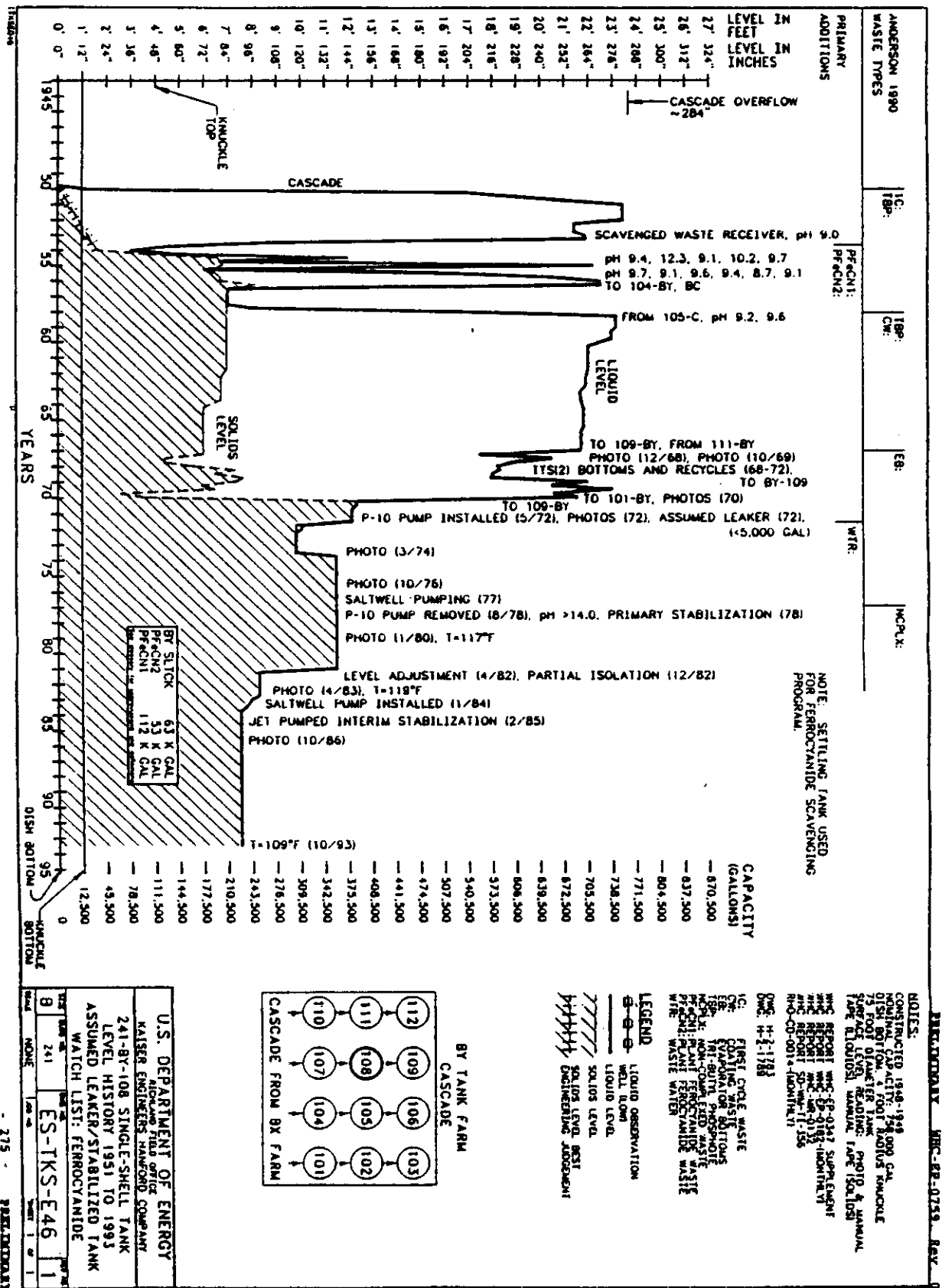
Included in this section are a physical description of tank BY-108, its process history, and recorded sampling events.

3.1 Configuration

Tank BY-108 is one of 16 single-shell tanks in the 200 East area BX Farm constructed during 1948-49. It is 23 meters (75 ft.) in diameter with a concave-shaped base and has a 2.87 million liter (758,000) tank capacity. The tank was used at one time as the secondary tank in a three tank cascade series which also included tanks BY-107 and BY-109.

3.2 Process History

Tank BY-108 received clarified first-cycle decontamination waste through BY-107 from the BX-107, BX-108, and BX-109 cascade from September 1950 to late 1952. In 1955, it was used as a tri-butyl phosphate scavenged waste receiver. In 1958, it received nearly 2,000,000 liters (530,000 gal.) of cladding waste transferred from tank C-105. The tank integrity was questioned and the supernatant was removed in 1970; it was later declared an assumed leaker in 1972. Saltwell pumping to remove interstitial liquid began in 1977. Interim stabilization was completed in February 1985.



3.3 Historical Sampling Events

No historical analytical data was found in the Tank Characterization Resource Center for the solid and liquid waste in tank BY-108. However, a type 2 vapor insitu sampling (ISS) event collected vapor space samples from tank BY-108 on March 28, 1994. Three SUMMA® canister samples were collected from the tank headspace and shipped to the Oregon Graduate Institute for analysis following Letter of Instruction guidelines (Osborne 1994b). Modified EPA TO-12 and TO-14 methods were applied to analyze the organic vapor. Analyses for nitrous oxide, hydrogen, and carbon monoxide were also performed. A data letter report, submitted to the TWRS Tank Vapor Issue Resolution Program, was produced as screening data and is not qualified data. These results and 10 of the 42 EPA TO-14 compounds detected are given in Table 1.

Results of an ambient air SUMMA® canister sample (field blank) collected upwind of BY-08 are 33 $\mu\text{g}/\text{m}^3$ of volatile organics following procedure EPA TO-12. Nitrous oxide, hydrogen, and carbon monoxide were not detected.

Table 1. Vapor Space Characterization Data for Tank BY-107.

Compound	Sample Identification Number		
	051	052	053
TNMHC ¹ by procedure TO-12, $\mu\text{g}/\text{m}^3$	610,810	584,400	587,164
Nitrous Oxide, ppmv	754	762	755
Hydrogen, ppmv	647	643	643
Carbon Monoxide, ppmv	< 5	< 5	< 5
EPA TO-14 Analytes, ppbv			
1,3-Butadiene	173	174	--
Freon 11	110	97	117
Vinylidenechloride	17	16	16
Freon 113	6	6	6
Benzene	91	91	86
Toluene	81	69	36
Ethyl Benzene	18	16	17
m&p-Xylene	56	56	55
1,1,2,2-Tetrachloroethane	2	2	2
o-Xylene	28	27	24

¹Total Non-Methane Hydrocarbons

3.4 Expected Tank Contents

Tank BY-108 is expected to have two primary layers of waste. The bottom layer should be ferrocyanide sludge generated from in-plant scavenging of waste from uranium recovery. This waste type has high concentrations of sodium and nitrate, and a very low concentration of plutonium. The upper layer is expected to be saltcake formed from in-tank solidification of slurry

product from the evaporator. Table 2 gives modeling estimates for the waste composition and inventory (Brevick et al. 1994).

Table 2. Single-Shell Tank BY-108 Solids Composite Inventory Estimate.

Physical Properties		
Total Solid Waste	1.27E+06 kg (228 kgal)	
Heat Load	1.02 kW (3.48E+03 BTU/hr)	
Bulk Density	1.47 g/cc	
Void Fraction	0.70	
Water Wt%	38.39	
TOC Wt% C (wet)	0.43	
Chemical Constituents	$\mu\text{g/g}$	kg
Na ⁺	1.32E+05	1.68E+05
Al ³⁺	1.91E+03	2.43E+03
Fe ³⁺ (total Fe)	1.41E+04	1.79E+04
Bi ³⁺	3.79E+04	4.82E+04
Ni ²⁺	4.10E+03	5.20E+03
K ⁺	19.27	24.46
OH ⁻	1.47E+04	1.86E+04
NO ₃ ⁻	1.68E+05	2.14E+05
NO ₂ ⁻	2.34E+03	2.97E+03
CO ₃ ²⁻	4.63E+03	5.88E+03
PO ₄ ³⁻	2.40E+04	3.05E+04
SO ₄ ²⁻	6.45E+04	8.19E+04
Si (as SiO ₃ ²⁻)	1.37E+04	1.74E+04
F ⁻	3.36E+03	4.26E+03
Cl ⁻	1.09E+02	1.39E+02
acetate ⁻	3.85E+02	4.89E+02
Fe(CN) ₆ ⁴⁻	1.22E+04	
Radionuclides	$\mu\text{g/g}$ or $\mu\text{Ci/g}$	Kg or Ci
Pu	2.35E-02 $\mu\text{Ci/g}$	0.50 kg
U	1.71E+03 $\mu\text{g/g}$	2.17E+03 kg
Cs	1.19E+02 $\mu\text{Ci/g}$	1.52E+05 Ci
Sr	36.21 $\mu\text{Ci/g}$	4.60E+04 Ci

3.4.1 Expected Tank Dome Space Vapor Composition

The quantification of the total volatile organic compounds by the EPA TO-12 procedure indicates a high level of organic vapors in the tank BY-108 vapor space, which suggests the presence of organics within the solid and liquid tank waste at a level greater than previously known.

The EPA TO-14 methodology was applied to obtain a GC/MS full scan chromatogram which indicated the presence of acetone, butanol, dodecane, tridecane, and other volatile organics. Other vapors of concern expected to be present in the vapor space are ammonia, methane, nitric oxide, and nitrogen dioxide.

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APPENDICES

TANK 241-BY-108 SAMPLING AND ANALYSIS PLAN

SAMPLE EVENT A

**VAPOR SAMPLING
IN FISCAL YEAR 1995**

SAMPLE EVENT A: VAPOR SAMPLING IN FISCAL YEAR 1995

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LIST OF ACRONYMS

BY-108	Tank 241-BY-108
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CGM	combustible gas meter
DOT	Department of Transportation
DQO	data quality objective
ECN	engineering change notice
EPA	Environmental Protection Agency
ESH&QA	Environmental Safety, Health, and Quality Assurance
FAS	Field Analytical Services
GC/MS	gas chromatography/mass spectrometry
IC	ion chromatography
IDLH	immediately dangerous to life and health
LFL	lower flammability limit
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory
ppbv	parts per billion by volume
ppmv	parts per million by volume
RCRA	Resource Conservation and Recovery Act
SML	Sampling and Mobile Laboratories
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TRP	Toxicology Review Panel
TO-12	EPA task order protocol 12
TO-14	EPA task order protocol 14
TOC	total organic carbon
TWRS	Tank Waste Remediation System
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

TANK 241-BY-108 VAPOR SPACE SAMPLING AND ANALYSIS PLAN

1.0 INTRODUCTION

Vapor samples are used to identify potential flammable and fugitive vapor emissions from the tanks which could become worker health and safety issues. Sampling of the vapor space will identify: 1) volatile compounds above the surface of the waste; and 2) the amount of gases generated by chemical or radiolytic reactions within the waste.

2.0 SCHEDULED SAMPLING EVENT

The following information provides the methodology and procedures to be used in the preparation, sample retrieval, transport, analysis, and reporting of results for vapor space samples retrieved from tank BY-108. Any decisions, observations, or deviations to this characterization plan made during sample receipt, preparation, and analysis shall be documented in the deliverable report.

2.1 Preparation of Sample Media Containers

The laboratory performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and/or selective sorbent sampling media) to Field Analytical Services (FAS) at least 48 hours in advance of the scheduled sampling date. Each sample media container shall be certified that preparation procedures were performed and it complies to cleanliness requirements. FAS shall provide sample identification numbers following the quality assurance/quality control format given in Section 3.1 and other label information to the laboratories as requested.

2.2 Flammability of Vapor Space Gases

Prior to performing intrusive work on a tank, an assessment of the flammability of the tank vapor space gases is required by standard WHC safety practices. Under present guidelines no operational or sampling activity is permitted if a single sample of the tank vapor fuel content, as measured with a combustible gas meter (CGM), is greater than 20% of the lower flammability limit (LFL). If this CGM sample has a total fuel content between 10% and 20% of the LFL, a vapor sampling activity may continue under CGM monitoring to better identify the hazard level. Under 10% of the LFL the tank is not considered a flammability problem and all scheduled work can proceed (Osborne et al. 1994a).

2.3 Sample Collection

In fiscal year 1995, the tank BY-108 vapor space shall be sampled through a heated probe in riser 1 using the vapor sampling system (VSS) in accordance with laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)". Table A.1 specifies the sample type, the type of collection media to be used, and the number of samples requested. Table A.2 provides a sequence of sampling activities and specifies the sample collection time and the flow rate through the sample collection tubes.

A cleanliness check shall be performed in accordance with procedure LO-080-450, Appendix C. Cleanliness of the VSS shall also be addressed by collecting ambient air SUMMA® samples prior to sampling the tanks using the following conditions: 1) with the VSS manifold and transfer lines fully heated; and 2) without the VSS, upwind of BY-108.

The GC/FID shall be used to monitor organic vapors during the sampling event. The GC/FID shall be operated in accordance with LO-080-450, Appendix D and Bellus (1993).

Table A.1. General Sampling Information

Sample Container	Prepared By	Preparation Procedure	Sample Type	Number of Samples
SUMMA®	PNL	PNL-TVP-002	Tank Air	6
SUMMA®	PNL	PNL-TVP-002	Ambient Air ³	2
Triple Sorbent Traps	ORNL	AC-OP-300-0907 CASD-AM-300-WP01 ⁴	Tank Air	12
	ORNL	AC-OP-300-0907	Field Blank	2
	ORNL	AC-OP-300-0907	Trip Blank	2
Sorbent Trap System for NH ₃ , NO ₂ , NO, H ₂ O	PNL	PNL-TVP-002	Tank Air	6
	PNL	PNL-TVP-002	Trip Blank	3
Tritium Trap	WHC	LA-548-111	Tank Air	1
HEPA Filters	WHC	N/A	Tank Air	4

³One sample taken through the VSS, one sample taken upwind of the tank.

⁴Preparation procedure for samples spiked with surrogate(s).

2.4 Radiation Screening and Sample Transport

All samples shall be stored at the 222-S Laboratory Annex following The sample receipt and control procedure PNL-TVP-07 while performing a radiological survey of the HEPA filters used in the VSS and the tritium trap sampler. This is necessary to comply with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria.

The HEPA filters used in the VSS shall be received by the 222-S Laboratory and analyzed for the acceptable specific (alpha, beta, gamma) activity levels given in Table A.3. The Tritium Trap shall be analyzed at the 222-S Laboratory for tritium using liquid scintillation counting to determine tritium activity.

The results from the radiation screening shall be submitted to and evaluated by Field Analytical Services to ensure the samples meet the analytical laboratory's acceptance criteria. Field Analytical Services shall provide a report to each analytical laboratory to identify the number of picocuries per sample (pCi/g of sample) for each sample that is submitted for analysis.

Table A.2. List of Samples and Activities.

SAMPLE CODE	SAMPLE/ACTIVITY DESCRIPTION	SAMPLER POSITION DURING COLLECTION	GAS FLOW RATE	SAMPLE DURATION
--	Purge VSS with ambient air ⁵	N/A	5,450 mL/min	30 min.
01	Collect ambient air sample SUMMA #1	Upwind of BY-108		1 min.
--	Collect GC sample and initiate GC run			
02	Collect ambient air sample SUMMA #2	Port 15		1 min.
--	Leak test	N/A		
--	Purge VSS with tank air	N/A	5,450 mL/min	30 min.
--	Measure tank pressure	N/A	N/A	N/A
03	Collect Tritium Trap	Sorbent line 8	200 mL/min	5 min.
--	Collect GC sample and initiate GC run			
04	Collect SUMMA #3	Port 11		1 min.
05	Collect SUMMA #4	Port 13		1 min.
06	Collect SUMMA #5	Port 15		1 min.
07	Collect SUMMA #6	Port 12		1 min.
08	Collect SUMMA #7	Port 14		1 min.
09	Collect SUMMA #8	Port 16		1 min.
10	Collect Triple Sorbent Trap (TST) sample #1	Sorbent line 9	25 mL/min	2 min.
11	Collect TST sample #2	Sorbent line 10	25 mL/min	2 min.
12	Collect TST sample #3	Sorbent line 8	25 mL/min	2 min.
13	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
14	Collect TST sample #4	Sorbent line 10	25 mL/min	2 min.
15	Collect TST sample #5	Sorbent line 9	50 mL/min	5 min.
16	Collect TST sample #6	Sorbent line 10	50 mL/min	5 min.
17	Collect TST sample #7	Sorbent line 8	50 mL/min	5 min.
18	Collect TST sample #8	Sorbent line 10	50 mL/min	5 min.
19	Collect TST sample #9	Sorbent line 9	100 mL/min	5 min.
20	Open, close, & store TST Field Blank #2	In VSS truck	0 mL/min	
21	Collect TST sample #10	Sorbent line 10	100 mL/min	5 min.
22	Collect TST sample #11	Sorbent line 8	100 mL/min	5 min.
23	Collect TST sample #12	Sorbent line 10	100 mL/min	5 min.
24, 25	Store TST Trip Blanks #1 & #2	None	None	None
26	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min.
27	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min.
28	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min.
29	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min.
30	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min.
31	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min.
32, 33, 34	Store NH ₃ /NO _x /H ₂ O Trap Trip Blanks #1, #2, & #3	None	None	None
35	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
36	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
37	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
38	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

⁵Not required if ambient air purge incorporated in VSS setup.

Table A.3. Limits For Acceptable Radionuclide Activity Levels.

Organization	Total α	Total B/y	Tritium	Units
PNL Analytical Chemistry Laboratory	≤ 100	≤ 400	--	pCi/g
Oak Ridge National Laboratory	≤ 135	≤ 450	--	pCi/g
WHC-CM-2-14 ⁶	≤ 60	≤ 200	--	pCi/g

⁶ Samples above DOT limits may be shipped as Limited Quantity of Radioactive Material in accordance with DOT approval.

Shipment of samples destined to the PNL 326 laboratory shall occur within 24 hours of the 222-S radiation screening. Trip blanks and field blanks are to accompany the waste samples to the laboratory. For specific information concerning sample and blank handling, custody, and transport refer to quality assurance/quality control requirements in Section 3.1.

2.5 Tank-Specific Analytical Procedures

2.5.1 Sampling, Isolation, and Analysis Scheme

A flowchart and narrative showing the sample collection, isolation, and analysis scheme is presented as Figure A.1. All samples are to be prepared and analyzed in accordance with this scheme. Sample receipt, custody, preparation, and analysis shall be performed in accordance with approved procedures.

Following a time period for evaluation of the laboratory report by the Toxicology Review Panel (TRP), and if deemed necessary by the TRP, requirements for further quantification and speciation shall be conveyed through a Letter of Instruction by the Characterization Program and/or revision to this Tank Characterization Plan.

2.5.2 Analytical Methods

Sample material retrieved from the tank BY-108 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons following modified EPA procedures TO-12 and TO-14. The sorbent traps contain analyte-specific sorbent media and shall be analyzed for these specific analytes. The triple sorbent traps contain sorbent media designed to allow a broad range of organic species to be retained. Table A.4 identifies the appropriate laboratory procedures used in each analysis.

Any analyses prescribed by this document, but not performed, shall be identified and justification for non-performance written in the appropriate data report. If there are insufficient samples to perform all requested analyses, Tank Vapor Safety Resolution Program personnel shall be contacted.

Figure A.1. Test Plan Outline and Flowchart for Tank Vapor Space Characterization.

- Step 1 Prepare sample and blank containers at contract laboratories. Label containers using sample identification numbers and sampling data provided by Field Analytical Services.
- Step 2 Ship containers to Field Analytical Services at least 4 days in advance of scheduled sampling event. Receipt and control of containers shall be guided by procedure PNL-TVP-07.
- Step 3 If tank is safe with regard to flammability, set up vapor sampling system (VSS) and collect samples following procedure LO-080-450 and guidelines in Table A.2.
- Step 4 Perform radiological field survey of HEPA filters. Ship to the 222-S Laboratory the vapor sample containers for locker storage, and the HEPA filters and Tritium Trap for radiological survey.
- Step 5 Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section 2.4).
- Step 6 If determined to be acceptable by offsite laboratory requirements and WHC-CM-2-14, ship samples and blanks following DOT requirements. If not acceptable to ship, maintain samples in storage and contact the J. W. Osborne of Vapor Issue Resolution Program for further direction.
- Step 7
 - A. SUMMA® Canisters (PNL): Perform EPA-T0-12. Perform full scan EPA-T0-14. Perform analyte-specific analysis for the following: H_2 , CO, N_2O , CH_4 , CO_2 .
 - B. Sorbent Traps (PNL): Perform gravimetric analysis for moisture. Perform selective electrode analysis for NH_3 . Analyze NO and NO_2 Traps.
 - C. Triple Sorbent Traps (ORNL): Perform organic vapor analysis.
- Step 8 Following the Section 6.0 reporting requirements, deliver a Format VI Report to the Vapor Issue Resolution Safety Program according to the contractual agreements.

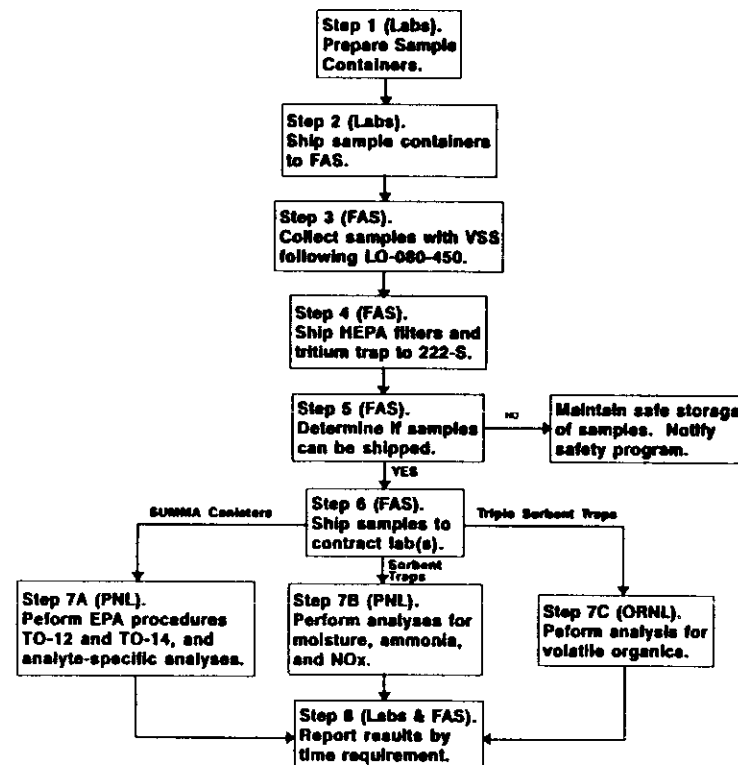


Table A.4. BY-108 Sample Chemical, Physical, and Radiological Analytical Requirements

PROJECT		BY-108 VAPOR		COMMENTS		REPORT FORMATS			NUMBER OF SAMPLE/BLANK CONTAINERS PROCESSED					
Plan Number		WHC-SD-WM-TP-275		Type 3 vapor sampling system (VSS) using heated vapor probes.		I		Early Notify	Organization		WHC	PNL	ORNL	TOTAL
Tank		BY-108				II		Process Control	SUMMA® Canister			6/2		8 ^a
Program Contact		J. W. Osborne J. L. Huckaby				III		Safety Screen	Sorbent Trap System ^b			6/3		9
TWRS Contact		B. C. Carpenter C. S. Homi				IV		Waste Management	Triple Sorbent Trap				12/4	16
Lab Project Coordinator		S. C. Goheen (PNL) R. A. Jenkins (ORNL)				V		RCRA Compliance	HEPA Filter		4			4
						VI		Special	Tritium Trap		1			1
PRIMARY ANALYSES						QUALITY CONTROL ^c			CRITERIA				REPORT FORMAT	
ANALYSIS METHOD	PRIMARY ANALYTE	PROCEDURE	LAB	SAMPLE PREP	SAMPLE CONTAINER	NO. OF SAMPLE	SURR SPIKE ^d	BLANK	ACTION LIMIT ^e	EXPECTED RANGE	PRECN	ACCURACY		
EPA TO-12	TNMHC	PNL-TVP-004	PNL	Direct	SUMMA®	3	none	2	N/A	500-700 mg/m ³	±10%	90-110%	VI	
EPA TO-14	Organic* Speciation	PNL-TVP-003 PNL-TVP-001	PNL	Direct	SUMMA®	3	none	2	≥ 4000 ppmv n-Butanol 50% IDLH for all others*	not available	±10%	90-110%	I, VI	
GC/TCD	CO ₂ CO CH ₄ H ₂ N ₂ O	PNL-TVP-006	PNL	Direct	SUMMA®	3	none	2	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available < 5 ppmv not available 500-600 ppmv 700-800 ppmv	±10% ±10% ±10% ±10%	90-110%	VI I, VI I, VI I, VI	
IC	NO NO ₂	PNL-ALO-009	PNL	H ₂ O Extraction	Sorbent Trap	4	none	1	≥ 150 ppmv ≥ 25 ppmv	not available not available	±10% ±10%	90-110%	I, VI I, VI	
Gravimetric	H ₂ O	PNL-ALO-009	PNL	Direct	Sorbent Trap	4	none	1	N/A	not available	±10%	90-110%	VI	
Selective Electrode	NH ₃	PNL-ALO-266	PNL	H ₂ O Extraction	Sorbent Trap	4	none	1	≥ 250 ppmv	not available	±10%	90-110%	I, VI	
GC/MS	Organics*	AC-MM-1-003153 AC-MM-1-003157	ORNL	Thermal Desorption	Triple Sorbent Trap	12	all	4 ^f	≥ 4000 ppmv n-Butanol 50% IDLH for all others*	not available	±10%	80-120%	I, VI	
Total α Total β Total γ	Radon Daughters	LA-508-110 LA-508-111 LA-508-162	WHC	Direct	HEPA Filter	4	N/A	N/A	≥60 pCi/g α ≥60 pCi/g α ≥200pCi/g β/γ	<60 pCi/g α <60 pCi/g α <200 pCi/g β/γ	±10% ±10% ±10%	90-110%	I, II	
Liq. Scin.	Tritium	LA-548-111	WHC	Direct	Tritium Trap	1	N/A	N/A	N/A	not available	±10%	N/A	II	
GC/FID	Organics	LO-080-450	FAS	Direct	On-line	N/A	N/A	N/A	N/A	N/A	N/A	N/A	II, VI	

N/A: Not Applicable

a Three canisters will be archived at PNL until arrangements can be made for transport and analytical work at the OGIST laboratory.

b System contains individual sorbent media sections for NO_x, NH₃, & H₂O.

c Multiple samples and blanks are taken.

d Samples are spiked with surrogates.

e Action required if any compound exceed 50% IDLH.

f Includes two trip and two field blanks.

*Acetone, acetonitrile, benzene, 1,3- butadiene, butanal, n-butanol, n-dodecane, n-hexane, methane, propanenitrile, tributyl phosphate, n-tridecane. Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall be reported following Format I.

3.0 QUALITY ASSURANCE/QUALITY CONTROL

This Tank Characterization Plan and resultant laboratory analysis data has been approved by the WHC Environmental Safety, Health, and Quality Assurance (ESH&QA) Program provided the following conditions are met.

- 1) Each laboratory has a quality assurance program that meets the requirement of DOE order 5700.6C.
- 2) Each analysis and media preparation procedure given in Tables A.1 and A.3 are documented by the laboratory and available to ESH&QA.
- 3) Any modifications made to, or deviations from, the prescribed procedures are documented and justified in the deliverable report.

ESH&QA will qualify laboratories for continued use by the program after receipt of the Laboratory quality assurance plans, and an audit and corrective action phase.

3.1 Sampling Operations

The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using unique sample label and identification numbers provided by Field Analytical Services. Each sample identification number shall have the following format:

SXXXX-WYY-LLL, where:

XXXX	=	unique number assigned to the sampling event,
W	=	a letter code indicating the day of a multi-day sampling event,
YY	=	a 2-digit sample code found in Table A.2, List of Sample and Activities, column one.
LLL	=	a special lab assigned code.

Once the sample collection media has been received by FAS from the laboratory, it shall remain in the physical control of the custodian, locked in a secure area, or prepared for shipping with tamper evident tape. The sample collection media shall also remain in a controlled area under conditions specified by the sample collection media supplier.

Applicable operating procedures for the tank BY-108 vapor space sampling activities are contained in work package ES-94-1159. Vapor samples, trip blanks, and field blanks are to be collected in accordance with Tables A.1 and A.2 and laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)" and shipped to the laboratory by Field Analytical Services in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

All sampling activities shall be documented in controlled field logbooks maintained by sampling personnel (Sampling and Mobile Laboratories) and shall contain, but are not limited to:

- 1) identification of tank and riser number and photographs of the sample location in which the sampling is conducted,

- 2) if any anomalies are observed, corresponding sample identification numbers, flow rates, pressures, temperatures, and other operational parameters affecting the sample,
- 3) any conditions that the sampler may observe during the sampling event (i. e., odors, nearby machinery in operation, etc.),
- 4) names and titles of personnel involved in the field activity and their responsibilities,
- 5) instrument calibration dates.

Sampling and Mobile Laboratories is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook and shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

3.2 Laboratory Operations

Prepared and labeled sample collection containers, trip blanks, and field blanks are supplied by the performing laboratories to Field Analytical Services. The SUMMA® canisters and Sorbent Trap Systems are prepared and certified following the laboratory quality control procedures identified in Table A.1. The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using sample label and identification numbers provided by Field Analytical Services.

The sample receipt and control procedures used in the Pacific Northwest Laboratory 326 Laboratory are reported by procedure PNL-TVP-07. Analyses performed at a laboratory shall be guided by a quality assurance program that meets the requirement of DOE order 5700.6C. The PNL 326 laboratory has an impact level II Laboratory Quality Assurance Plan (Barnes 1994).

Method specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, standards) are identified in Table A.4. If no criteria are provided in Table A.4, the performing laboratory shall perform to its quality assurance plan(s).

Due to the developmental work being done with the analysis procedures and potential sample differences (between tanks), changes in procedures may be needed. These changes must be documented in controlled notebooks referenced in the deliverable reports to ensure traceability.

4.0 ORGANIZATION

The organization and responsibility of key personnel involved in this tank BY-108 vapor sampling project are listed in Table A.5.

Table A.5. Tank BY-108 Project Key Personnel List.

Individual(s)	Organization	Responsibility
S. C. Goheen	Pacific Northwest Laboratory	Project Manager for Vapor Sample Characterization
R. A. Jenkins	Oak Ridge National Laboratory	Project Manager for Vapor Sample Characterization
B. C. Carpenter C. S. Homi	TWRS Characterization Support	BY-108 Tank Characterization Plan Engineers
J. L. Huckaby	TWRS Tank Vapor Issue Resolution Program	Vapor Issue Resolution Engineer
H. Babad	TWRS Characterization Program	Tank Safety Screening Scientist
R. D. Mahon	Field Analytical Services	Sampling and Mobile Laboratories Vapor Sampling Program Lead
E. H. Neilsen	Waste Tank Safety Engineering	Vapor Sampling Cognizant Engineer
D. R. Carls	Industrial Hygiene and Safety Program	Industrial Hygiene Point of Contact if Action Limit is Exceeded (FAX 372-3522)
East Area Shift Operations Manager	Tank Farm Operations	East Tank Farm Point of Contact if Action Limit is Exceeded (373-2689)

5.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

5.1 Exceptions to DQO Requirements

The determination of the flammability of tank vapor space gases will not be made *during* this sampling event. This determination is performed and reported *prior* to the sampling event by health physics personnel during periodic tank flammability testing. Once determined to be safe in regard to flammability, the tank is regarded as safe for a period of 6 months. During this period normal tank operations and sampling is permitted, following which a new flammability test may be performed.

5.2 Clarifications and Assumptions

Trip Blanks and Field Blanks

Trip Blanks are sampling devices prepared and handled in the same manner as samples, except that they are never opened in the field. Field Blanks are sampling devices prepared and handled in the same manner as the samples, but no tank samples are collected with them. Laboratories supplying blanks may opt to analyze only 1 trip blank unless it is determined to be contaminated, in which case all trip blanks are to be analyzed.

Sample Custodian

The sample custodian is the designated FAS cognizant scientist or assisting scientific technician, lead sampler, or laboratory scientist or technician who signs the *received by* block on the chain of custody. Transfer of custodianship occurs when the custodian signs the *relinquished by* block on the chain of custody and releases the sample(s) to the new custodian signator.

Physical Control

Physical control of a sample includes being in the sight of the custodian, in a room which shall signal an alarm when entered, or locked in a cabinet.

6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank BY-108 vapors shall reported as Format VI (Section 6.3). All reports shall be submitted to J. W. Osborne of the Tank Vapor Safety Resolution Program. In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section 6.2. Table A.4 identifies the primary analytes of concern and expected to be present in the vapor space of tank BY-108. Any analyte exceeding the notification limit prescribed in Table A.4 shall be reported as Format I (Section 6.1). Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall also be reported following Format I. Other report recipients are identified in the following sections. Additional information regarding reporting formats is given in Schreiber (1994).

6.1 Format I Reporting

Table A.4 contains the notification limits for specific analytes. Analytes that exceed notification limits defined in the DQO processes shall be reported by the Project Manager, delegate, or Health Physics Management by calling the East Area Shift Manager of Tank Farm Operations at (509) 373-2689 immediately. This verbal communication must be followed within 3 working days by written communication to J. W. Osborne of the Tank Vapor Issue Resolution Program, D. R. Carls in the Industrial Hygiene and Safety Program, and D. R. Bratzel of the Characterization Program, documenting the observation(s). A further review of the data, including quality control results and additional analyses for verification of the exceeded analyte, may be contracted between the performing laboratory and the contacts above.

6.2 Format II Reporting

Results of the 222-S Laboratory's radiological survey shall be reported by Sampling and Mobile Laboratories as Format II to the analytical laboratories listing the picocuries per sample (pCi/g of sample) for each sample submitted for analysis. This Format II report should also provide the sample collection sequence and volumes, verification of trip and field blank use, and any anomalous sampling conditions to accompany, if possible, the shipment of samples. Alternatively, this sampling report may be transmitted by FAX to the analytical laboratories within 48 hours after the samples have been shipped.

6.3 Format VI Reporting

The final sampling report from Sampling and Mobile Laboratories shall be a WHC supporting document, with sponsor-limited release. It should include:

- 1) A description of sampling equipment used;
- 2) a description of sampling quality controls applied (e.g., leak and cleanliness tests of the sampling manifold, system temperature and pressure monitoring/alarms, instrument calibration details);
- 3) sampling event chronology and sample collection schedule (complete list of samples, by ID#, time collected, flow rates, etc.);
- 4) any industrial hygiene tank monitoring data collected before or during sampling event;
- 5) an evaluation of sources of sampling errors;
- 6) sample radiation screening results;
- 7) sample storage and shipment details; and
- 8) copies of all chain-of-custody forms.

Reports by the analytical laboratories shall be suitable for public distribution. To the extent applicable, the reports should include:

- 1) A summary of analytical results;
- 2) a description of sample device preparation (and manufacture if appropriate), citing procedures and logbooks used;
- 3) references providing traceability of sample device cleanliness;
- 4) a brief description of analytical methods, with procedures cited;
- 5) a brief explanation of how analytical systems control was demonstrably maintained;
- 6) a brief description of sample storage and shipment conditions, citing procedures and logbooks used;
- 7) a listing of analytes of quantitation (target analytes), with analytical method detection limit, range for which instrumentation is calibrated, number of calibration points used, and statistical data on linearity of calibration;
- 8) quantitative analytical results, expressed as dimensionless (ppmv or ppbv) concentration, and mass concentration ($\mu\text{g}/\text{m}^3$, mg/L, etc., calculated at 0 °C and 1 atm) of target analytes (identified by name and Chemical Abstract Service number) in each tank air sample;
- 9) tentative identification and semi-quantitative analytical results, expressed in both mass and dimensionless concentrations (if possible) of non-target organic analytes (identified by name and Chemical Abstract Service number) in each organic vapor sample;
- 10) a statistical summary (i.e., mean, standard deviation) for multiple analyses and/or multiple samples for all analytes (positively and

- tentatively identified compounds) in both mass and dimensionless concentrations (if possible);
- 11) a summary of all exceptional conditions, such as deviations from procedure or protocol, results obtained outside of instrument calibration range, sorbent trap breakthrough of analytes, or poor surrogate recoveries; and
- 12) chain-of-custody forms attached.

7.0 CHANGE CONTROL

Under certain circumstances, it may become necessary for the performing laboratory to make decisions concerning a sample without review of the data by the customer or the Characterization Program. These changes shall be brought to the attention of the project manager and the Characterization Program as quickly as possible and documented accordingly. Changes must be justified in their documentation. Changes may be documented through the use of internal change notices or analytical deviation reports for minor, low-impact changes. All significant changes (such as changes in scope) shall be documented by Characterization Support via an Engineering Change Notice to this Tank Characterization Plan. All changes shall also be clearly documented in the final data package.

Additional analysis of sample material from this vapor space characterization project at the request of the Characterization Program shall be performed according to a revision of this Tank Characterization Plan.

8.0 REFERENCES

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- Keller, K. K., 1994, *Quality Assurance Project Plan for Tank Vapor Characterization*, WHC-SD-WM-QAPP-013, Rev.2, Westinghouse Hanford Company, Richland, Washington.
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- Schreiber, R. D., 1994, *Revised Interim Tank Characterization Plan Guidance*, (letter 7E720-94-121 to C. S. Haller, May 13), Westinghouse Hanford Company, Richland, Washington.
- Whelan, T. E., 1994, *TWRS Characterization Program Quality Assurance Program Plan*, WHC-SD-WM-QAPP-025, Westinghouse Hanford Company, Richland, WA.